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Photochemically and thermally induced radical promoted cationic polymerization using an allylic sulfonium salt

Selcuk Denizligil and Yusuf Yagci*
Department of Chemistry, Istanbul Technical University, Maslak 80626, Istanbul, Turkey

and Ciaran McArdle
Loctite International, Tallaght Business Park, Whitestown Industrial Estate, Dublin 24, Ireland

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The photochemically and thermally generated radical promoted cationic polymerization of epoxides such as cyclohexene oxide (CHO) and vinyl monomers such as n-butyl vinyl ether (BVE) and *N*-vinyl carbazole (NVC) is reported. This system consists of an allylic sulfonium salt, and photochemical and thermal radical initiators. Photoinduced radical generation was achieved with benzoin (B) and 2,4,6-trimethylbenzoyl diphenylacylphosphine oxide (TMDPO) which absorb light at wavelengths where the sulfonium salt is transparent. A feasible mechanism involves radical addition to the allylic double bond and subsequent fragmentation to yield reactive species capable of initiating cationic polymerization. An alternative mechanism which involves the oxidation of electron donor radicals is also discussed. The enhanced activity of the thermal initiators, 2,2′-azobisisobutyronitrile (AIBN), benzoyl peroxide (BP) and phenylazotriphenylmethane (PAT) was confirmed in the polymerization of CHO initiated by the sulfonium salt at 60°C.

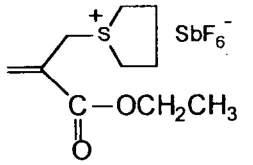
(Keywords: cationic polymerization; allylic sulfonium salt; radical addition)

INTRODUCTION

There has been a growing interest in the industrial application of cationic polymerization processes over the last two decades[1]. Commercially important and well studied cationic photoinitiators are onium salts[2], namely diaryliodonium and triarylsulfonium salts. Recently, pyridinium[3] and mixed ligand arene cyclopentadienyl metal salts[4] have been developed as alternative cationic photoinitiators.

Diaryliodonium and triarylsulfonium salts have poor spectral sensitivity at wavelengths where commercial lamps emit light. Photosensitizers[5] and free-radical photoinitiators[6] have been successfully employed to extend their spectral response to longer wavelengths. Electron transfer from the excited photosensitizer or photogenerated electron donor radicals to the onium salts results in the formation of reactive species which are capable of initiating the cationic polymerization of related monomers (*Scheme 1*).

In marked contrast to the behaviour of diaryliodonium salts simple triarylsulfonium salts such as triphenyl sulfonium do not participate in electron transfer reactions with free radicals due to their unfavourable reduction potentials (see Table 2, below). Structurally complex sulfonium salts, such as the dialkylphenacyl sulfonium and 4-(phenylthio)phenyl-diphenyl sulfonium salts, although somewhat less effective, can also be used[7] in this manner. In this present work, the allyl sulfonium salt which has the following structure was examined with respect to its reactivity towards photochemically and thermally generated radicals.



Ethyl-α-(tetrahydrothiophenium methyl) acrylate hexafluoroantimonate (ETM$^+$SbF$_6^-$)

$$\mathrm{PS} \xrightarrow{h\nu} \mathrm{PS}^{*} \qquad (1)$$

$$\mathrm{PS}^{*} + \mathrm{On}^{+} \longrightarrow \mathrm{PS}^{+\cdot} + \mathrm{On}^{\cdot} \qquad (2)$$

$$\mathrm{PS}^{+\cdot} + \mathrm{Monomer} \longrightarrow \mathrm{Polymer} \qquad (3)$$

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{R}^{\cdot} \qquad (4)$$

$$\mathrm{R}^{\cdot} + \mathrm{On}^{+} \longrightarrow \mathrm{R}^{+} + \mathrm{On}^{\cdot} \qquad (5)$$

$$\mathrm{R}^{+} + \mathrm{Monomer} \longrightarrow \mathrm{Polymer} \qquad (6)$$

PS=Photosensitizer
PI=Photoinitiator

Scheme 1

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* To whom correspondence should be addressed

It will be shown later that cations formed with the aid of ETM^+ are capable of initiating the polymerization of cyclic ethers such as cyclohexene oxide (CHO) and vinyl monomers such as n-butyl vinyl ether (BVE). It turned out that the radical promoted photoinitiation process using ETM^+ is different to those proposed for iodonium and pyridinium salts.

EXPERIMENTAL

Materials

Ethyl-α-(tetrahydrothiophenium methyl)acrylate hexafluoroantimonate ($ETM^+SbF_6^-$) was prepared by the stoichiometric, dropwise addition of tetrahydrothiophene to ethyl-α-(bromomethyl)acrylate at room temperature with stirring. The acrylic substrate was prepared by the method of Vilieras and Rambaud[8]. The bromide salt (ETM^+Br^-) was isolated by filtration, washed copiously with diethyl ether, dried and then taken up in aqueous solution. To this aqueous solution was added an aqueous solution of sodium hexafluoroantimonate. On mixing the two clear solutions, $ETM^+SbF_6^-$ precipitated out. The i.r. and n.m.r. data of all of the intermediate and final products were in agreement with the target molecule.

Monomers and solvents were purified by conventional drying and distillation procedures. 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TMDPO), from BASF, was recrystallized twice from ethanol/diethyl ether, benzoin (B) (Merck) and 2,2′-azobisisobutyronitrile (AIBN) (Fluka) were recrystallized from ethanol, and benzoyl peroxide (BP) (Fluka) was recrystallized from diethyl ether. Phenylazotriphenylmethane (PAT) was prepared as described previously[9].

Polymerization

Photopolymerization. Solutions of monomer, sulfonium salt and initiator were prepared separately. Appropriate amounts of the solutions were transferred to a Pyrex tube, and the mixtures were then bubbled through with argon before irradiation by a xenon lamp equipped with a monochromator.

Thermal polymerization. Solutions of monomer, sulfonium salt and initiator were mixed in Pyrex tubes that were closed with a Teflon stopcock after bubbling through with argon. For the polymerization reaction, the tubes were immersed for a given time in an oil bath which was kept at 60°C.

Characterization

Polymers were obtained from the reaction mixture by precipitation with methanol. In some cases methanol-soluble fractions were analysed with a Varian 3700 gas chromatograph which was connected to a mass spectrometer. U.v.–vis. spectra were recorded on a Perkin–Elmer Lambda 2 spectrophotometer. Gel permeation chromatography (g.p.c.) analyses were performed with a set-up consisting of a Waters pump and four Ultrastyragel columns with porosities 10^5, 10^4, 10^3 and 500 Å. THF was used as the eluent, at a flow rate of $1\ ml\ min^{-1}$ and detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

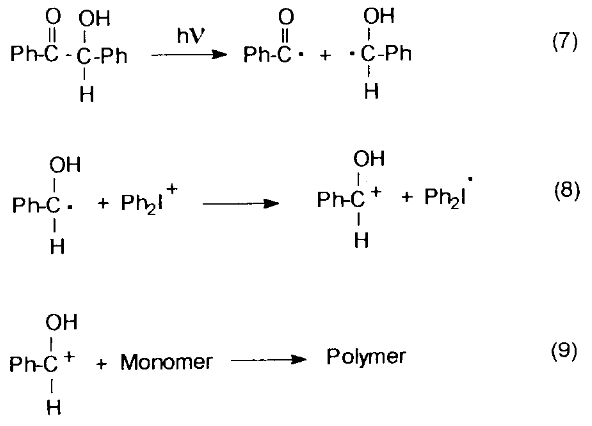
RESULTS AND DISCUSSION

Reactions of radicals generated by photolysis

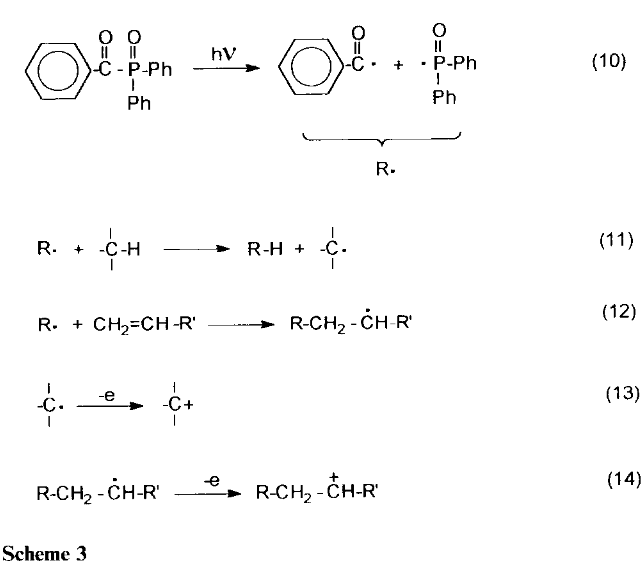
Photochemical sources of free radicals that promote[3,10] cationic polymerization in the presence of onium salts include benzoin (B) and derivatives, acylphosphine oxides, vinyl halides, polysilanes and benzophenone–hydrogen donor couples. Of these, benzoin derivatives are the most important class on account of their high quantum efficiency of generating free-radicals and the ease of oxidation of these radicals, as shown below for the benzoin–diphenyl iodonium salt system (*Scheme 2*).

Acylphosphine oxides[11,12] are another class of free-radical photoinitiators which also participate in free-radical promoted cationic polymerization. It was demonstrated[12] that neither benzoyl nor phosphonyl radicals react with onium ions, but instead they abstract hydrogen from suitable donors or add to the monomers. The resulting carbon centred radicals are converted into carbocations by reaction with the onium ions (*Scheme 3*).

For these reasons, we employed benzoin and 2,4,6-trimethylbenzoyl diphenylphosphonyloxide (TMDPO) as light absorbing chromophores, yielding oxidizable and non-oxidizable radicals, respectively. The absorption spectra of benzoin (B), TMDPO and ETM^+ are shown in *Figure 1*. Since the sulfonium salt does not



Scheme 2



Scheme 3

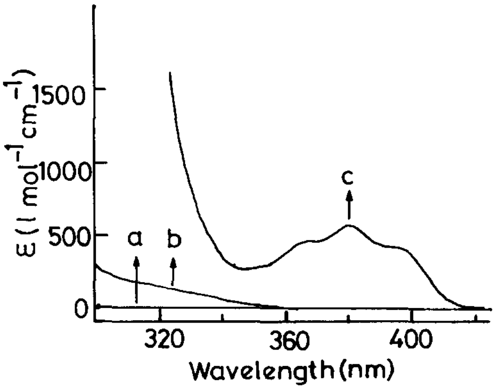
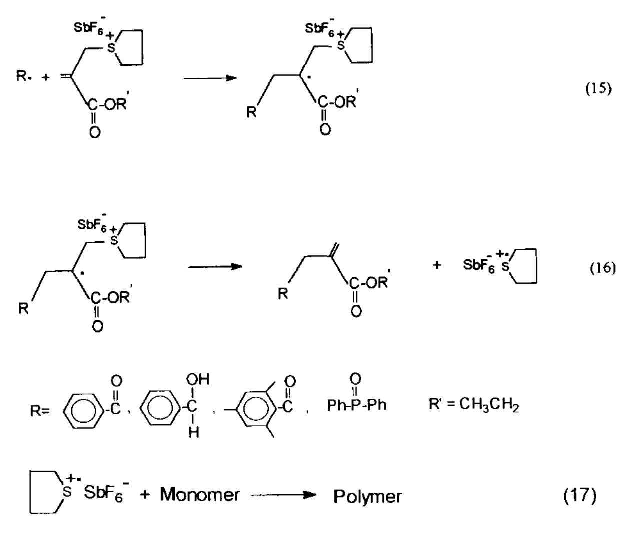
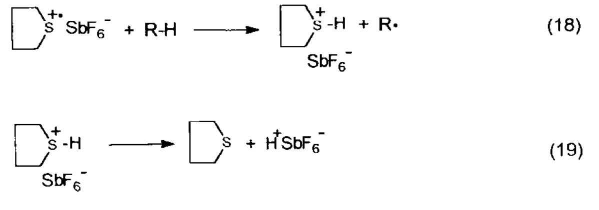


Figure 1 Optical absorption spectra recorded in dichloromethane at room temperature for: (a) ETM$^+$SbF$_6^-$; (b) benzoin; (c) TMDPO

absorb at $\lambda > 300$ nm, all irradiations were performed at $\lambda_{\rm inc} > 340$ nm. As can be seen from *Table 1*, cyclohexene oxide (CHO) was polymerized quite effectively with B and TMPDO as free-radical sources. In the absence of these compounds the photolysis of an ETM$^+$ solution containing CHO in CH_2Cl_2 at either $\lambda = 340$ or 380 nm failed to produce any precipitated polymer. A mechanism for initiation, consistent with a recent report[13] on the reaction of free radicals with olefins containing leaving groups in the allylic position, is shown below (*Scheme 4*). The resulting sulfonium radical cations may directly initiate cationic polymerization, as was proposed by Ledwith *et al.*[14] for polymerization initiated by the direct irradiation of sulfonium salts.



Scheme 4



Scheme 5

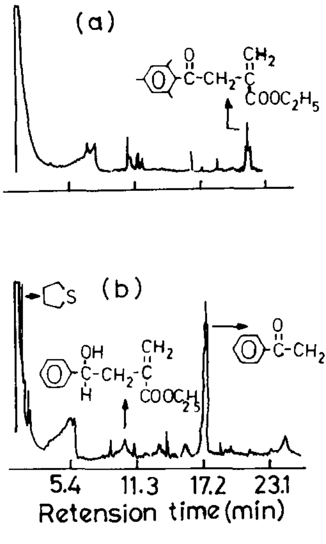


Figure 2 Gas chromatograms of the methanol-soluble products formed during the photopolymerization of CHO initiated by: (a) TMDPO/ETM$^+$; (b) B/ETM$^+$

Alternatively, the radical cations may abstract hydrogen from the solvent or the monomer, with the resulting intermediate dissociating as shown in *Scheme 5*. Protons generated in this way add to the monomer, thus forming species capable of initiating the cationic polymerization:

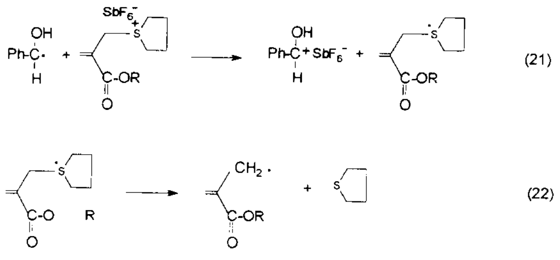
$$H^+ + \text{Monomer} \rightarrow \text{Polymer} \qquad (20)$$

Additional support for the initiation by radical addition and fragmentation processes in the polymerization was obtained by analysing the remaining methanol-soluble products of the polymerization mixture. Typical gas chromatograms of these products are presented in *Figure 2*. These show, apart from solvent, monomer and starting compounds, various other peaks corresponding to the photoproducts. Notably, peaks for the unsaturated compounds originating from the addition and fragmentation steps (equations (15) and (16)) were detected in both cases. Interestingly, tetrahydrothiophene (THT) was not detected in the case of TMDPO

Table 1 Photoinitiated polymerization of various monomers using TMPO in the presence of ETM$^+$, in CH_2Cl_2 at room temperature

Monomer	Time (min)	[M] (mol l^{-1})	[ETM$^+$] × 10^3 (mol l^{-1})	[TMPO] × 10^3 (mol l^{-1})	Conversion (%)	M_n (g mol^{-1})	M_w/M_n
CHO	30	6.46	5	5	27.4	9099	2.08
CHO	30	6.46	5	–	0	–	–
BVE	30	2.2	5	5	74.02	13964	1.79
BVE	30	2.2	5	–	52.4	19111	2.46
NVC	5	1	5	5	49.07	45803	2.53
4-VCHD[a]	20	5.2	5	5	100	–	–

[a] 4-Vinyl cyclohexene dioxide



Scheme 6

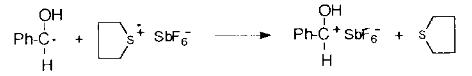
which indicates that the mechanisms according to equations (15)–(17) play an important role with respect to the initiation of these cationic polymerizations. It is interesting to note that, in the case of benzoin, the amount of the hydroxybenzyl radical adduct is considerably less than that of the benzoyl radical. This behaviour may be due to participation of these radicals in electron transfer reactions. It is expected that they are oxidized to the corresponding cation by interaction with the ground state sulfonium ion, according to the reactions shown in *Scheme 6*.

In principal, electron transfer from radical to onium ion is feasible if the free energy, ΔG, is negative, where ΔG is given by the following equation[15]:

$$\Delta G = E_{1/2}^{\text{ox}}(\text{R}\cdot) - E_{1/2}^{\text{red}}(\text{On}^+) \qquad (23)$$

where $E_{1/2}^{\text{ox}}(\text{R}\cdot)$ and $E_{1/2}^{\text{red}}(\text{On}^+)$ represent the oxidation potential of the free radical and the reduction potential of the onium salt, respectively. As can be seen from *Table 2* the value of $E_{1/2}^{\text{red}}$ for the allylic sulfonium salt is lower than that of the pyridinium salt which undergoes efficient redox reactions with carbon centred free radicals. It is, therefore, expected that the favourable redox potential allows this salt to accept an electron from the photogenerated radicals, thus initiating the polymerization.

Similar electron transfer mechanisms may be written for initiation by the cation radical fragments produced in the photoinduced addition and fragmentation steps.



(24)

Identical redox reactions were observed with complex sulfonium salts[14]. At present it is difficult to distinguish which mechanism is operative for the initiation, although formation of THT confirms exclusively the existence of an electron transfer reaction.

In addition to CHO, BVE, *N*-vinylcarbazole (NVC) and 4-vinyl cyclohexene dioxide (4-VCHD) were also examined. These monomers also polymerized readily in solutions containing a sulfonium salt and TMDPO. Typical results are shown in *Table 3*. Although initiation occurred even without a free-radical initiator in the case of BVE, the presence of TMDPO strongly enhanced the efficiency, indicating reaction between the salt and the photogenerated radical. Intense coloration during polymerization of BVE initiated by the TMPDO–sulfonium salt (*Figure 3*) gives evidence for the different initiating mechanisms for direct and radical induced polymerizations. In the case of 4-VCHD, which possesses two epoxide groups an insoluble network polymer was readily formed.

Table 2 Reduction potentials of representative cationic salts and their capability of initiating free-radical promoted cationic polymerization

Cationic salt	$E_{1/2}^{\text{red}}$ *versus* SCE[a]	Polymerization	Ref.
Ph_2I^+	−0.2	Yes	16
ETM^+	−0.58	Yes	This work
EMP^{+b}	−0.7	Yes	9
Ph_3S^+	−1.06	No	17

[a] Standard calomel electrode

[b] EMP^+, *N*-ethoxy-2-methylpyridinium

Table 3 Photoinitiated polymerization of CHO using free-radical photoinitiators (PIs) in the presence of ETM^+ in CH_2Cl_2 at room temperature[a]

PI	λ_{inc} (nm)	Conversion (%)	M_n[b]	M_w/M_n
TMPO	380	27.4	9099	2.08
Benzoin	340	71.1	15023	1.99

[a] Polymerization time = 30 min; [CHO] = 6.46 mol l^{-1}, [PI] = 5×10^{-3} mol l^{-1}, and [ETM^+] = 5×10^{-3} mol l^{-1}

[b] Determined by g.p.c. according to polystyrene standards

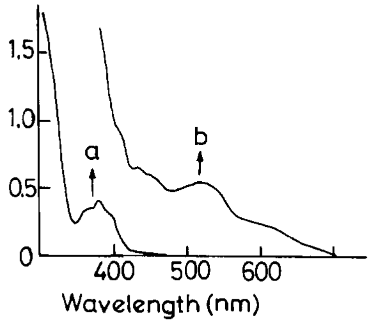


Figure 3 Optical absorption spectra of the polymerization mixture of BVE in dichloromethane: (a) before; (b) after 30 min irradiation. Conditions: [BVE] = 2.2 mol l^{-1}; [TMDPO] = 5×10^{-3} mol l^{-1}; [ETM^+] = 5×10^{-3} mol l^{-1}; λ = 380 nm; polymerization time = 30 min

Reactions of radicals generated by thermolysis

It was shown by Endo and coworkers[18] that benzylic-type sulfonium salts are efficient thermally latent initiators in the cationic ring-opening polymerization of bicyclo *o*-esters, spiro *o*-carbonates and epoxides, and also in the vinyl polymerization of styrenes. Allylic sulfonium salts also act as latent initiators, and can initiate cationic polymerization by heating under given conditions (see *Table 4*). The initiating species are expected to be allylic cations, consistent with the mechanism proposed for benzylic sulfonium salts.

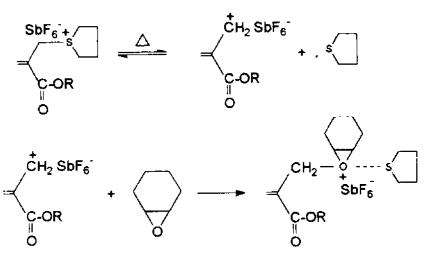
Table 4 Thermally induced cationic polymerization of CHO using the allylsulfonium salt in CH_2Cl_2[a]

Thermal source[b]	Time (min)	Conversion (%)	M_n (g mol^{-1})
None	30	15.60	15864
BP	30	67.27	19250
PAT	1	80	13095
AIBN	30	46.22	26925

[a] Polymerization time, 30 min; temperature 60°C; [CHO] = 6.46 mol l^{-1}; [ETM^+] = 5×10^{-3} mol l^{-1}

[b] [Thermal source] = 5×10^{-3} mol l^{-1}

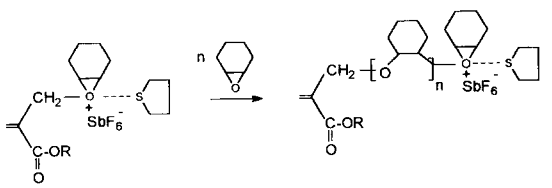
Initiation.



(25)

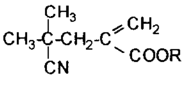
(26)

Propagation.



(27)

Addition of thermal free-radical initiators significantly accelerated the polymerization of CHO. Radicals originating from the thermolysis of benzoyl peroxide (BP) and 2,2′-azobisisobutyronitrile (AIBN) are unreactive towards onium salts[6,9]. Oxidizable radicals can only be generated in the presence of hydrogen donors, by hydrogen abstraction. In our case, however, initiating species are produced by a radical addition–fragmentation mechanism (see *Scheme 4* where R = $(CH_3)_2CCN$ for AIBN, and PhCOO or Ph for BP) without the requirement of any additional hydrogen donor. The gas chromatogram of the products of the remaining polymerization mixture after precipitation into methanol (*Figure 4*) shows the presence of THT and an addition–fragmentation product with the following structure:



$$CH_3\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}C(=CH_2)COOR$$

This indicates that both direct and radical induced mechanisms are operative under these experimental conditions. In the case of phenylazotriphenylmethane (PAT), however, a different situation was encountered. This compound decomposes both thermally and also photochemically to yield triphenylmethyl and phenyl radicals:

$$Ph\text{-}N{=}N\text{-}CPh_3 \xrightarrow{\Delta \text{ or } h\nu} Ph\cdot + N_2 + Ph_3C\cdot \qquad (28)$$

The triphenylmethyl radical is a stable radical and can easily be oxidized to the corresponding carbocation by cationic salts with the appropriate reduction potentials. Apparently the PAT/ETM$^+$ system initiated an explosive polymerization reaction of CHO within 1 min (see *Table 4*). In contrast to the triphenylsulfonium salt, the oxidative nature of the allylic salt, which is related to the substantial difference in the reduction potential, was proven by the formation of a stable triphenylmethyl cation (*Figure 5*) upon the thermolysis of PAT/ETM$^+$ according to analogous reactions that have been described for the hydroxybenzyl radical (*vide ante*). It should be pointed out, however, that we cannot rule out an addition–fragmentation-type initiation by phenyl radicals which are also formed during the thermolysis process.

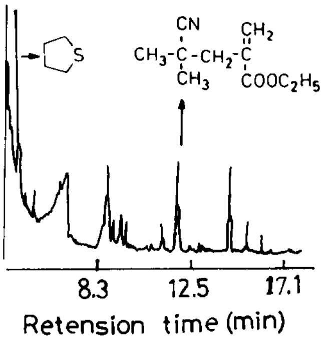


Figure 4 Gas chromatogram of the methanol-soluble product formed during thermal polymerization of CHO initiated by AIBN/ETM$^+$ at 60°C

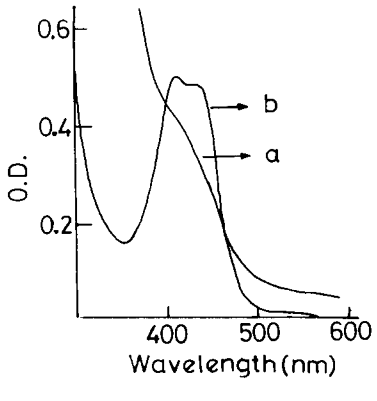


Figure 5 Optical absorption spectra of a solution containing 5×10^{-3} mol l^{-1} of PAT and 5×10^{-3} mol l^{-1} of ETM$^+$ in dichloromethane after heating at 60°C for 50 min: (a) before heating; (b) after heating

CONCLUSIONS

It is clear that in a system consisting of a photoinitiator, a co-initiator, and an allylic sulfonium salt with a non-nucleophilic anion, the photoinitiator functions as a photon acceptor and produces radicals. The sulfonium salt is responsible for generating reactive cations by either the so-called addition–fragmentation mechanism or by oxidizing some of the radicals that are formed.

An initiating system containing such a sulfonium salt offers several unique advantages, as follows:

(1) Spectral sensitivity can be adjusted by selecting a photoinitiator with the required maxima.
(2) Radicals formed do not need to be electron donors, i.e. any radicals which are capable of adding double bonds may be employed. In the case of non-oxidizable radicals, additional hydrogen donors are not required to produce the initiating species. This possibility is not offered by any other existing cationic salts, including iodonium and pyridinium salts which are known to be strong oxidants.
(3) Thermally produced radicals, regardless of their structure, are also capable of reacting with the sulfonium salt to generate initiating species.

Further studies are now in progress to use various photosensitizers and visible dyes in conjunction with the sulfonium salt for the initiation of cationic polymerization, and this work will be reported elsewhere.

ACKNOWLEDGMENTS

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REFERENCES

1 Pappas, S. P. in 'Photopolymerization Science and Technology' (Ed. N. S. Allen), Elsevier, London, 1989, p. 55
2 Crivello, J. V. *Adv. Polym. Sci.* 1984, **62**, 1
3 For a recent review, see Yagci, Y. and Schnabel, W. *Macromol. Symp.* 1994, **85**, 115
4 Meier, K. and Zweifel, H. J. *J. Radiat. Curing* 1986, **13**, 26
5 Pappas, S. P., Pappas, B. C., Gatechair, L. R., Jilek, J. H. and Schanabel, W. *Polym. Photochem.* 1984, **5**, 1
6 Ledwith, A. *Polymer* 1978, **19**, 1217
7 Crivello, J. V. and Lee, J. L. *Polym. J.* 1985, **17**, 73
8 Vilieras, J. and Rambaud, M. *Synthesis* 1982, 924
9 Böttcher, A., Hasebe, K., Hizal, G., Yagci, Y., Stelberg, P. and Schnabel, W. *Polymer* 1991, **32**, 2289
10 Yagci, Y. and Schnabel, W. *Makromol. Chem. Macromol. Symp.* 1992, **60**, 133
11 Yagci, Y. and Schnabel, W. *Makromol. Chem. Rapid Commun.* 1987, **8**, 209
12 Yagci, Y., Borberly, J. and Schnabel, W. *Eur. Polym. J.* 1989, **25**, 129
13 Mejis, G. F., Rizzardo, E. and Thang, S. H. *Polym. Bull.* 1990, **24**, 501
14 Ledwith, A., Al-Kass, S. and Hulme-Lowe, A. in 'Cationic Polymerization and Related Process' (Ed. E. J. Goethalls), Academic, London, 1984, p. 275
15 Rehm, D. and Weller, A. *Ber. Bunsenges Phys. Chem.* 1969, **73**, 834
16 Ptitsyna, O. A., Levashova, T. W. and Butin, K. P. *Dokl. Akad. Nauk. SSSR* 1971, **201**, 372
17 Grimshaw, J. in 'The Chemistry of Sulphonium Groups' (Eds C. J. M. Stirling and S. Patai), Wiley, New York, 1981, p. 129
18 Kikkawa, A., Takata, T. and Endo, T. *Makromol. Chem.* 1991, **192**, 655, and references cited therein